

PATENT SPECIFICATION

(11) 1 394 353

1 394 353

- (21) Application No. 30483/73 (22) Filed 27 June 1973
 (61) Patent of Addition to 1 347 051 dated 19 April 1971
 (31) Convention Application No. 267 664 (32) Filed 29 June 1972 in
 (33) United States of America (US)
 (44) Complete Specification published 14 May 1975
 (51) INT CL² A61K 7/06
 (52) Index at acceptance ASB 774

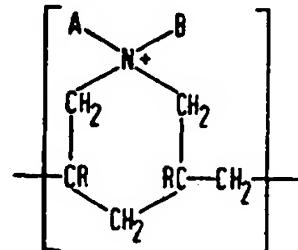


(54) HAIR TREATING COMPOSITION

(71) We, THE GILLETTE COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Prudential Tower Building, Boston, Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to hair-treating compositions for bleaching, waving or straightening, or coloring (dyeing) hair, and more specifically to such compositions containing high molecular weight water soluble polymers having a multiplicity of amino or of quaternary ammonium groups.

In Specification 1,347,051, we have described and claimed cosmetic compositions for application to hair, which comprise (1) a hair waving or straightening lotion comprising a keratin reducing agent, or a neutraliser therefor containing an oxidizing agent or (2) a hair bleaching composition comprising an oxidizing agent or (3) a hair dye composition comprising an oxidative or non-oxidative dye, and (4) a high molecular weight water soluble quaternary ammonium polymer having a molecular chain containing units of the formula:



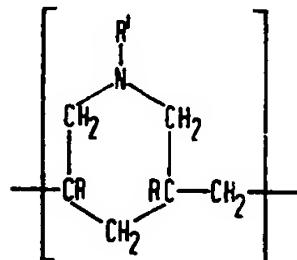
wherein R is hydrogen or methyl and A and B are independently alkyl groups having from one to twenty-two carbon atoms, lower

hydroxyalkyl groups, or lower alkyl groups containing terminal amido groups, or wherein A and B taken together with N are piperidinyl or morpholinyl groups. Reference should be made to Specification 1,347,051 for further details.

We have now found that cosmetic compositions containing certain high molecular weight water-soluble polymers similar to those employed in the compositions claimed in Specification 1,347,051 are also advantageously employed in the treatment of hair.

According to the invention, there is provided a hair-treating composition for bleaching, waving or straightening, or coloring hair, which comprises, in addition to a bleaching agent, a waving or straightening agent, or a coloring agent, an aqueous solution of a water soluble polymer having a molecular weight from 20,000 to 3,000,000, the polymer being

(1) a homopolymer or copolymer containing units of the following formula:



wherein R is hydrogen or methyl; R' is hydrogen, or an alkyl group having one to twenty-two carbon atoms, or a lower hydroxyalkyl group having from one to five carbon atoms, or a lower alkyl group containing a terminal amido group; or an acid addition salt thereof with a non-toxic, cosmetically-acceptable acid; or

(2) a copolymer of acrylamide or diacetone acrylamide and at least one monomer which provides, in the resulting copolymer, units of the following formula:

40

45

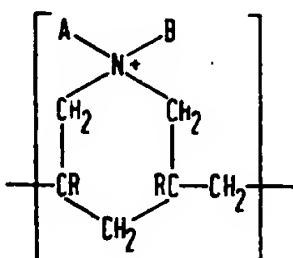
50

55

60

65

70



- wherein R is as defined above and A and B are independently alkyl groups having from one to twenty-two carbon atoms, lower hydroxyalkyl groups, or lower alkyl groups containing terminal amido groups, or wherein A and B taken together with N are piperidinyl or morpholinyl groups; the amount of said polymer being from 0.05% to 40% by weight of the total aqueous composition.
- The invention also comprises a process of bleaching, waving or straightening, or coloring hair, which comprises applying thereto a composition of the invention.
- The polymers used according to the invention are incorporated in the hair treating composition itself instead of being used in the form of separate solutions separately applied. The hair treating composition in each case includes in addition to water and the water-soluble polymer (as defined above) a coloring agent i.e. a hair dye or hair dye precursor; or a hair waving or straightening agent such as a reducing agent capable of breaking the disulfide linkages in hair keratin; or a peroxide such as hydrogen peroxide in the case of hair bleaching compositions or neutralizing compositions (for use in conjunction with waving or straightening compositions). Also present in the case of the hair coloring and hair bleaching compositions are a surface active agent such as a soap or detergent and sufficient water-miscible aliphatic hydroxylated solvent (or a mixture of such solvent with a water-soluble salt inert to the ingredients and to hair) to maintain the composition homogeneous i.e. in a single phase.
- The polymers are equally effective when an anionic surface active agent such as soap, etc. is present as when only cationic, nonionic, or ampholytic agents are present despite the fact that ionic interaction would be expected to lead to the formation of an inactive and insoluble catan wax. The polymer can be used effectively in amounts ranging upwardly from 0.05% to 40% by weight of the total composition. If the composition is supplied in concentrated form, that is the polymer concentration is near the upper limit of 40% by weight, it is generally desirable to dilute it with water to a polymer content of 0.5 to 15% by weight before use. The compositions in which the polymers may be effectively employed may vary widely in acid or base content, having a pH, when in water, from 1.5 to 11.5. The polymers are effective to alter

the surface characteristics of the hair and maintain the desired conditioned effect even though the application of the composition is followed, intentionally or unintentionally, by a water rinse. Indeed, the conditioning effect produced by incorporating these polymers in a hair treating composition is remarkably durable, persisting in many cases through several successive rinses and even through successive washings with a conventional detergent or shampoo composition. This is true even in the case of hair coloring and hair bleaching compositions which contain soap or detergent which in itself would be expected to remove the polymer even if no shampoo were subsequently used.

In the hair coloring compositions of the present invention the coloring agents may be any of the known acidic, basic, or disperse dyes or oxidation dye intermediates; they may be present in any effective amount ranging from 0.03 to 10% by weight of the total composition, depending on the type of dye and the desired color result, as is well known to those skilled in the art. When the coloring agent is an oxidative dye intermediate, it is usually desirable to mix with the composition before applying it to the hair an oxidizing agent such as hydrogen peroxide, sodium peroxide, urea hydrogen peroxide or the like, in accordance with conventional practice, in an amount effective to develop the desired color.

The hair bleaching compositions contain in aqueous solution an oxidizing agent such as hydrogen peroxide or urea hydrogen peroxide together with conventional stabilizers such as phenacetin and/or sodium stannate together, if desired, with a suitable conventional buffer to maintain the pH at the desired level of 2.5 to 6.5. The amount of oxidizing agent, in accordance with conventional practice, may be from 0.5 to 20% by weight of the total composition.

The hair waving and straightening compositions of the present invention contain aqueous solutions of reducing agents capable of reducing the disulfide linkages in hair keratin, of which many are well known such as water soluble mercaptans e.g. sodium or ammonium thioglycolate, magnesium thioglycolate, thioglycerol, sodium or potassium borohydride, and sodium or ammonium sulfite. The amount of such reducing agent, as is well known, may be from 0.5 to 10% by weight of the total composition. A variety of conventional additives for such compositions may also be present.

The neutralizer compositions of the present invention, which are used for applying to the waved or straightened hair to restore the disulfide linkages in the hair keratin, contain in aqueous solution any of the oxidizing agents conventionally employed for this purpose, such as hydrogen peroxide, urea hydrogen peroxide, sodium carbonate peroxide, sodium or potas-

60

65

70

75

80

85

90

95

100

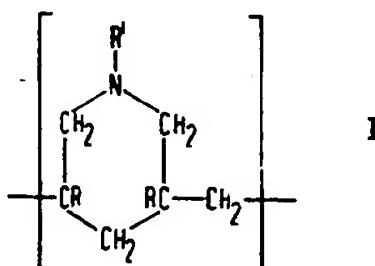
105

110

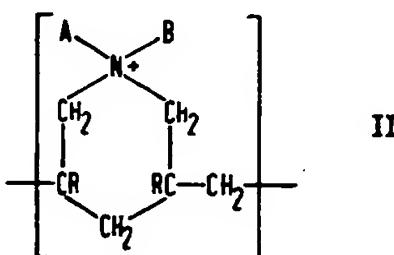
115

120

- sium bromate, sodium perborate, or sodium hypochlorite; the neutralizer compositions used with sulfite waving or straightening compositions may simply contain sesquicarbonate instead of an oxidizing agent.
- The surface active agent present as an essential ingredient of the hair coloring or hair bleaching composition may be a soap, that is, an alkali metal, ammonium or amine salt of a long chain aliphatic acid, particularly a fatty acid, such as the sodium, potassium, lithium or ammonium salts or the salts of such amines as mono-, di-, or tri-ethanolamine, 2 - amino - 1 - butanol, 2 - amino-2 - methyl - 1 propanol, diethylamine, mono- and diisopropanolamine, polyglycolamine, N-ethylmorpholine with such acids as capric, undecylic, lauric, myristic, palmitic, stearic, oleic, linoleic, ricinoleic, dimer or trimer acids produced by polymerization of C₁₈ fatty acids, hydrogenated rosin acids, lanolin acids, phenyl-stearic acid, coconut fatty acids, tallow fatty acids, or castor fatty acids including hydroxy-ricinoleic acid and the like. The surface active agent may also be an anionic material such as sodium di-(2-ethylhexyl) phosphate, dioctyl sodium sulfosuccinate, sodium dodecylbenzenesulfonate, sodium lauryl sulfate, or disodium ethoxylated alcohol half ester of sulfosuccinic acid. Cationic surface active agents can also be used, such as stearyldimethylbenzylammonium chloride, stearic amino-amide, dimethyldialkylammonium chlorides in which each alkyl group has from 8 to 18 carbon atoms, polyethoxylated quaternary ammonium salts, amidoamine oxide derivative of lauric acid, or cetylpyridinium chloride. Among nonionic surface active agents which can be used are various condensates of alkylene oxides, for example ethylene oxide or propylene oxide, with other molecules, each condensate molecule containing from 5 to 500 alkylene oxide units, such as octylphenoxy-polyethoxyethanol, condensates of ethylene oxide with hydrophobic bases formed by condensing propylene oxide with propylene glycol, mono- and diglycerides of long chain fatty acids, sorbitan esters of long chain fatty acids, polyoxyethylene sorbitan monolaurate, monopalmitate or mono-stearate, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, lauric diethanolamide, dimethyloctadecylamine oxide, nonyl-phenylpolyethylene glycol ether, ethylene oxide condensates with long chain fatty amides, acetylated lanolin alcohols, or coconut fatty acid alkanolamides. Amphoteric surface active agents useful in the compositions of the present invention include imidazoline derivatives made by condensing polyamines with long chain fatty acids including lauric, capric, oleic and stearic sold under the trade name Miranol in the form of various salts such as the potassium, sodium, mono-, di-, or triethanolamine or isopropanolamine salts, N-coco-*beta*-aminopropionic acid or its sodium salt, disodium N-lauryl-*beta*-iminodipropionate, N-lauryl/myristyl - *beta* - aminopropionic acid, or a complex polyalkylamido imidazolinium sulfate sold under the trade name Soromine CAZ-75. Any of these surface active agents may be present as an optional ingredient in the hair waving or straightening compositions or neutralizing compositions of the present invention. The surface active agents can be used in amounts from 0.1 to 50% by weight of the total composition, preferably from 0.3 to 25% by weight.
- When a surface active agent is present in any of the compositions, there must also be present sufficient water miscible hydroxylated organic primarily aliphatic solvent, or a mixture of such solvent with inert water-soluble salt, to solubilize all of the ingredients. Among suitable solvents are ethanol, isopropanol, benzyl alcohol, hexylene glycol, hexanol, 2-methylpentanol, 2-ethylbutanol, diethylene glycol, tetraethylene glycol, propylene glycol, 1,5-pentanediol, polyethylene glycol, glycol ethers such as 2-ethoxyethanol, 2-phenoxyethanol, monoethylether of diethylene glycol, monobutyl ether of diethylene glycol, monobutyl ether of diethylene glycol, monobutyl ether of 1,2-propanediol, monomethyl ether of dipropylene glycol, or 1-butoxyethoxy-2-propanol. The minimum amount of such solvent needed to ensure homogeneity will vary depending upon the identity and quantity of other ingredients present but in general may range from 1 to 90% by weight of the total composition.
- The water soluble salts which can be used in conjunction with the hydroxyl-containing solvent to increase its effectiveness include those which are chemically inert to the remaining ingredients of the composition as well as to the hair such as the sodium, potassium, lithium, ammonium or lower alkanolamine chlorides, bromides, sulfates, or acetates. They can be used in amounts from 0.01 to 15% by weight of the total composition, preferably from 0.05 to 5% by weight.
- The polymers useful in the present invention are high molecular weight water-soluble amino homopolymers and copolymers and quaternary ammonium copolymers having as constituents of the chain or backbone of the polymer molecule (apart from end groups which terminate each such chain and which have no important effect upon the properties and characteristics of the polymer) units as follows:
- (1) homopolymers and copolymers containing units of the following formula:

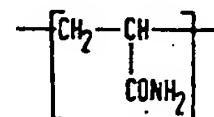


where R is hydrogen or methyl; R' is hydrogen, or an alkyl group having one to twenty-two carbon atoms, or a lower hydroxyalkyl group having from one to five carbon atoms, or a lower alkyl group containing a terminal amido group such as beta-propionamido; or
 5 (2) copolymers of acrylamide or diacetone acrylamide and at least one monomer which provides, in the resulting copolymer, units of the following formula:

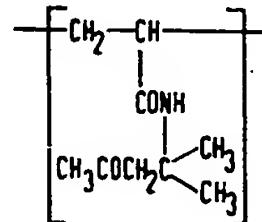


15 wherein R is as defined above and wherein A and B are independently (i.e. either both the same or different) alkyl groups having one to twenty-two carbon atoms, lower hydroxyalkyl groups having from one to five carbon atoms, and lower alkyl groups containing terminal amido groups such as beta-propionamido; or wherein A and B together with N are piperidinyl or morpholinyl groups. Salts of Polymer 1 such as the hydrochloride, hydrobromide or sulfate are the full equivalent of Polymer 1. The preferred homopolymers and copolymers (1) and copolymers (2) are those in which R is hydrogen. Also, preferred copolymers (2) are those in which A and B are independently lower alkyl groups having from 1 to 5 carbon atoms or in which A and B form, together with the nitrogen atom, a piperidinium or a morpholinium group. These linear homopolymers and copolymers have a molecular weight from about 20,000 to 3,000,000. In the case of homopolymers (1), all of the units in the polymer chain are identical, while in the case of copolymers (1), the units, while having the structure defined above, are not all identical to each other. Copolymers (2) contain structures derived from acrylamide or diacetone acrylamide as described below and may contain different units of the above-defined structure. Any of a wide variety of non-toxic, cosmetically acceptable anions, organic as well as inorganic, may be present in the polymer and associated with the quaternary ammonium

cationic groups, among which are, for example, acetate, borate, bromide, chloride, citrate, tartrate, bisulfate, bisulfite, sulfate, phosphate, and succinate. The homopolymers and copolymers of Formula I can be prepared as described in United States Patent 2,926,161 by polymerizing the appropriate diallylamine or amine salt. The copolymers of Formula II can be made by copolymerizing diallyldialkylammonium chloride or bromide or other appropriate diallyl monomeric ammonium salts with acrylamide or diacetone acrylamide using a free radical generating polymerization catalyst such as a peroxide, then using an anion exchange column technique for exchanging the anion, if desired. Such techniques are described in United States Patents 3,288,770 and 3,412,019. If a polymer of a chloride is dissolved in an aqueous solution or in a cosmetic base containing salts of any other anions, of course, the resulting solution contains both anions, each being associated to some extent with the quaternary ammonium groups of the polymer. The polymer units derived from acrylamide have the structure



while those derived from diacetone acrylamide have the structure



The amounts of these acrylamide-type monomers incorporated in the copolymer may vary from 5% to 95% by weight of the total monomers; the copolymers can be made by subjecting the mixture of monomers to the same polymerization conditions as used in making the homopolymers. It generally makes no difference, so far as the present invention is concerned, whether the polymer or copolymer containing a particular desired anion or combination of anions is prepared in pure form before being mixed with the hair treating composition or whether the desired anions are introduced into the composition in the form of other salts. It is usually most convenient to employ the least expensive salt of the polymer which is readily available, regardless of the anion which it contains, and add the desired anions in the form of other less expensive salts. Hair treating compositions, as is well known, contain any of a wide variety of non-toxic anions, numerous

examples of which are given herein.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only:

- 5 In order to ascertain the presence of the conditioning effect in the Examples, the following test was performed. Tresses were prepared using hair that has been bleached and waved. This type of hair is difficult to comb either wet or dry and represents a realistic standard for the evaluation of conditioning treatments. An untreated tress was marked as a control and was evaluated both for wet and dry combing properties. A number of tresses from the same hair lot (to eliminate variations from lot to lot) were then subjected to the hair treating composition to be tested. The evaluations were made by a panel of cosmetic scientists or beauty operators. The tresses were combed and ranked on a 1 to 5 scale, where 1 is the poorest and 5 is the best. The change in rating from the control value was an indication of the effectiveness of the conditioning treatment. Persistence of high ratings after a series of shampoos indicated the continued existence of conditioning on the tress. The ratings reported in the following Examples are based on the above scale and are for wet combings unless specified otherwise.

EXAMPLE 1.
The following compositions (Table I) were prepared, the compositions being suitable for

use as hair dyes on addition of the desired dye. The compositions were then mixed with an aqueous 16% hydrogen peroxide solution in the proportion of 3.5 parts by weight of the composition to 1.0 part of peroxide solution, and the mixture left in contact with hair tresses, one virgin hair which had never been bleached or chemically waved, the other bleached and waved hair, for 20 minutes at room temperature, then rinsed.

Each hair tress was then rated for condition with the results set forth in Table II. In this case the hair tresses were rated both while wet (WC) and after drying (DC) as well as being rated again after one shampoo and rinse (1S) and after three (3S).

TABLE I.

Ingredient	Per cent by Weight
Oleic acid	8.7
Monoethanolamine	5.0
Triton X-100 (Octylphenoxy polyethoxy (9-10)ethanol)	1.0
Triton X-35 (Octylphenoxy polyethoxy (3-4)ethanol)	5.0
Isopropanol	25.0
EDTA	0.05
Sodium sulfite	0.05
Polymer	1.0
Water	q.s.

"Triton" is a Trade Mark.

TABLE II

Hair Condition

	Virgin				Bleached/Waved			
	WC	DC	WC(1S)	WC(3S)	WC	DC	WC(1S)	WC(3S)
Polydiallylamine hydrochloride	4.5	3.0	4.5	4.0	4.3	3.5	4.0	3.0
None	3.5	3.0	3.5	3.5	2.5	4.0	2.5	2.5

EXAMPLE 2.

Hair bleaching compositions were prepared by mixing with one part by weight of a 16% aqueous hydrogen peroxide solution 3.5 parts of each of several compositions having the following recipe, the polymer in each case being different as listed in Table III.

Recipe.

Ingredient	Weight Per Cent
Oleic acid	9.0
Monoethanolamine	5.1
Octylphenoxy polyethoxy ethanol (9-10)	1.0
Octylphenoxy polyethoxy ethanol (3-4)	5.0
Isopropanol	15-37
Cationic polymer	1.0
Water q.s. to	100.0

TABLE III.

- Polydiallylamine hydrochloride
Copolymer (50:50) of dimethyldiallylammonium chloride and acrylamide
5 Copolymer (75:25) of dimethyldiallylammonium chloride and acrylamide
Copolymer (27:63) of dimethyldiallylammonium chloride and acrylamide
10 Copolymer (13:87) of dimethyldiallylammonium chloride and acrylamide
Copolymer (7:93) of dimethyldiallylammonium chloride and acrylamide
Copolymer (90:10) of dimethyldiallylammonium chloride and diacetone acrylamide
15 Copolymer (95:5) of dimethyldiallylammonium chloride and diacetone acrylamide

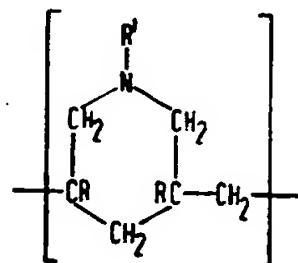
The compositions were evaluated by applying them to tresses of both virgin and bleached/waved hair and allowing them to stand for 20 minutes. After rinsing and shampooing, the tresses displayed the same superior condition as observed in Example 1, in contrast to the undesirable condition of tresses treated with similar compositions omitting the polymer.

25

WHAT WE CLAIM IS:—

1. A hair-treating composition for bleaching, waving or straightening, or coloring hair, which comprises, in addition to a bleaching agent, a waving or straightening agent, or a coloring agent, an aqueous solution of a water soluble polymer having a molecular weight from 20,000 to 3,000,000, the polymer being
30 (1) a homopolymer or copolymer containing units of the following formula:

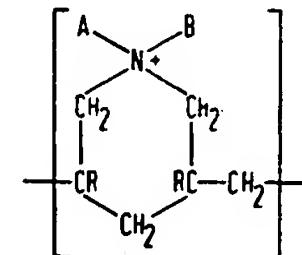
35



40

wherein R is hydrogen or methyl; R' is hydrogen, or an alkyl group having one to twenty-two carbon atoms, or a lower hydroxyalkyl group having from one to five carbon atoms, or a lower alkyl group containing a terminal amido group; or an acid addition salt thereof with a non-toxic cosmetically acceptable acid;
(2) a copolymer of acrylamide or di-

acetone acrylamide and at least one monomer which provides, in the resulting copolymer, units of the following formula:



wherein R is as defined above and A and B are independently alkyl groups having from one to twenty-two carbon atoms, lower hydroxyalkyl groups, or lower alkyl groups containing terminal amido groups, or wherein A and B taken together with N are piperidinyl or morpholinyl groups; the amount of said polymer being from 0.05% to 40% by weight of the total aqueous composition.

2. A composition as claimed in claim 1, in which A and B are both methyl groups.

3. A composition as claimed in claim 1, in which A and B are both ethyl groups.

4. A composition as claimed in claim 1, in which the homopolymer or copolymer (1) is one in which R' is β -propionamido.

5. A composition as claimed in any one of the preceding claims, which contains from 0.5 to 20% by weight of a surface active agent.

6. A composition as claimed in claim 1 or 2, in which the copolymer (2) contains up to 95% by weight of the total of units derived from acrylamide or diacetone acrylamide.

7. A process of bleaching, waving or straightening or coloring hair, which comprises applying thereto a composition as defined in any one of the preceding claims.

8. A package comprising a composition as claimed in any one of claims 1 to 6, together with a propellant liquid in a pressure container.

9. A hair-treating composition according to claim 1, substantially as hereinbefore described in Example 1 or 2.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303/306 High Holborn,
London, W.C.1.